

Aircraft measurements of nitrogen oxides, ozone, and carbon monoxide during MINOS 2001: distributions and correlation analyses

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Abstract

We present mean altitude profiles of NO_x , NO_y , O_3 , and CO as measured by the DLR Falcon aircraft during the MINOS 2001 campaign over the Mediterranean in August 2001 and compare the data with results from other aircraft campaigns, namely the SIL 1996 (North Atlantic flight corridor), the POLINAT-2 (North Atlantic flight corridor), and the EXPORT 2000 (central Europe) campaigns. The MINOS NO_y , O_3 , and CO mixing ratios in the free troposphere, especially between 4–8 km, are very similar to those measured during the EXPORT 2000 campaign. However, compared to the other campaigns the MINOS O_3 and CO were significantly higher in the boundary layer, by about 20 ppbV and 50 ppbV, respectively. In the second part of the paper the $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$, $\Delta[\text{O}_3]/\Delta[\text{CO}]$, $\Delta[\text{CO}]/\Delta[\text{NO}_y]$, and $\Delta[\text{NO}_x]/\Delta[\text{NO}_y]$ trace gas correlations were calculated for the MINOS 2001 campaign. It was found that, within the scatter of the data, the overall average altitude profiles of the correlations compared well with data from a literature survey. The analysis of the mean vertical correlation profiles as measured during MINOS 2001 does therefore not single out special meteorological conditions and air mass origins over the Mediterranean in summer but reflects a more general condition of the free troposphere in the northern hemisphere. Correlation analyses for single flights at different altitudes, however, unambiguously identify air masses influenced by the stratosphere, whereas pollution plumes could only be identified with the help of back trajectories.

1 Introduction

Extensive measurements of trace gases and aerosol parameters were performed on board the DLR research aircraft Falcon during the Mediterranean Intensive Oxidant Study (MINOS) over the eastern Mediterranean Sea out of Heraklion, Crete, in August 2001. The objective of the MINOS campaign was to study the main processes involved in the Mediterranean pollution build-up, i.e. (a) the transport of pollution from

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Europe and from remote sources, (b) the chemical mechanisms that contribute to the build-up of oxidants and aerosols, and (c) the export of pollutants to the global environment, e.g. towards south-east Asia, see also Lelieveld et al. (2002), and <http://www.mpch-mainz.mpg.de/~reus/minos/>. During the campaign fourteen measurement flights plus ferry flights from and to Germany were made, comprising measurements of e.g. NO, NO_y (=NO+NO₂+HNO₃+HONO+PAN+NO₃+...), O₃, J(NO₂), CO, CH₄, CO₂, PAN, aerosol parameters, selected carbonyl compounds, alcohols, and hydrocarbons. Supplementary ground-based observations were made during the campaign from Finokalia, Crete.

In an overview of MINOS, presented in Lelieveld et al. (2002) air pollution in different altitude regimes over the Mediterranean in summer was traced to several source regions, see also Millan et al. (1997, 2002). While the boundary layer is mainly influenced by northerly winds carrying West- and East-European emissions, the composition of the free troposphere is dominated by a mixture of Asian, North Atlantic, and North American air masses from the west. In the upper troposphere outflow from the Asian monsoon is brought into the Mediterranean from the east. This is also illustrated in Fig. 1 which shows a qualitative analysis of the air mass origins as an altitude plot over Crete during August 2001, based on the 6-hourly output from model runs with ECHAM4 (T63) (Roelofs et al., this issue). The “lifetime” of the color encoded idealized tracers was set to 14 days. It should be noted that the contour lines in Fig. 1 are arbitrary and give no information about total values of tracers. According to the model results the overall picture of the origins in August 2001 suggests a strong influence of European pollution (yellow) on the Crete planetary boundary layer (PLB) up to about 2 km altitude. In the free troposphere (≈3–8 km) a layer with tracers of stratospheric origin (blue) is mixed with North American (red) and North Atlantic (green) tracers. During most of the campaign the upper tropospheric air was found to be strongly influenced by monsoon outflow being uplifted from the PBL over Asia (orange). This very sharp layering weakened after 15 August 2001, and eventually broke up until the end of the campaign, see also Roelofs et al., this issue.

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One of the main objectives of this paper is to present and discuss mean vertical profiles of (a) the trace gas mixing ratios and (b) the trace gas correlations derived from the MINOS 2001 aircraft dataset, in support of the analysis of trace gas source regions and types.

Mean altitude profiles of the NO_x, NO_y, O₃, and CO volume mixing ratios measured during the fourteen MINOS 2001 flights will be shown in Sect. 3.1. These data will be discussed and compared with data from former studies, i.e. the SIL 1996 (“Schadstoffe in der Luftfahrt”), the POLINAT-2 (“Pollution from Aircraft in the North Atlantic Flight Corridor”), and the EXPORT 2000 campaigns which were carried out in other regions and during different seasons.

In Sect. 3.2 the $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$, $\Delta[\text{O}_3]/\Delta[\text{CO}]$, $\Delta[\text{CO}]/\Delta[\text{NO}_y]$, and $[\text{NO}_x]/\Delta[\text{NO}_y]$ correlations obtained during MINOS 2001 will be analysed. These correlations refer to (a) mean altitude profiles during the campaign, and (b) single observed plumes, along the flight tracks as time series, and as altitude profiles from single measurement flights. Case studies of single flights together with back trajectory analyses will be shown in this section. Finally, the MINOS 2001 correlations will be compared with data from earlier studies.

2 Experimental

The in situ aircraft measurements of NO, NO_y, the photolysis frequency of NO₂ (JNO₂), ozone (DLR), carbon monoxide (MPI-CH), and the meteorological parameters (DLR) during MINOS 2001 were performed on board the DLR Falcon. Detailed descriptions of the equipment are reported elsewhere (Ziereis et al., 1999, 2000a, 2000b; Junkermann et al., 1989, Volz-Thomas et al., 1996; Wienhold et al., 1998).

Briefly, NO is measured with a well characterized chemiluminescence detector (CLD). NO_y is measured with a second CLD in combination with an Au converter heated to 300°C with CO (0.2%) as the reduction agent. Calibration of the CLDs is performed before the flights using a diluted mixture of 2.97 ppmV ±1% NO in N₂

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(Messer-Griesheim) with purified air. The pressure dependent efficiency of the NO_y conversion is determined with a known amount of NO₂ generated from gas phase titration of NO with O₃ and is 0.92–0.99 for the pressure range discussed in this study. The detection limits of the instruments are 5 pptV for NO, and 15 pptV for NO_y. The accuracies of the measurements are 5% and 12% for NO and NO_y, respectively.

The photolysis frequency J(NO₂) is obtained from the sum of two filter radiometers (Meteo Consult GmbH) with 2π viewing geometry. One of the radiometers is installed on top of the aircraft, the second on the downward facing side of the aircraft body. The detectors have been optimized for flight applications (Volz-Thomas et al., 1996) and have recently been characterized in our laboratory (Hauser, 2002). The overall uncertainty of the J(NO₂) measurements is about 17%.

To obtain the NO_x (=NO+NO₂) mixing ratios the NO₂ concentrations were computed assuming simple photostationary steady state conditions (e.g. Leighton 1961; Atkinson 2000)

$$[\text{NO}_2] = \frac{k(\text{NO} + \text{O}_3)}{J(\text{NO}_2)} \times [\text{NO}] \times [\text{O}_3], \quad (1)$$

where the temperature dependent reaction rate coefficient $k(\text{NO} + \text{O}_3)$ was calculated from the data given in Sander et al. (2000). The overall uncertainty of the nitrogen dioxide mixing ratios depends on the experimental uncertainties of NO and O₃, J(NO₂), $k(\text{NO} + \text{O}_3)$, and on the unknown amount of NO₂ produced by molecules other than O₃ (e.g. RO₂) and is estimated to be about 25%.

UV-absorption measurements of ozone were performed with a modified TE 49 instrument (Thermo Environmental) calibrated with a O₃ 41M ozone generator (ANSYCO) which is frequently calibrated against a standard device from the Global Atmosphere Watch system (GAW) (<http://www.wmo.ch>). The accuracy of the ozone measurements is 5%, the time resolution is 4 s.

Carbon monoxide measurements were performed using a tunable diode laser (TD-LAS) instrument with a precision of 1.5 ppbV (1σ) and a calibration accuracy of 1.5%

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for 1 s integration times (Wienhold et al., 1998). Since the TDLAS measured two additional trace gases with approximately the same time resolution the CO data were obtained every 4–6 s.

To reduce the number of experimental data and to obtain a dataset on the same time scale 10 s averages of all quantities were calculated.

3 Results and discussion

3.1 Altitude profiles of trace gases

3.1.1 Altitude profiles of NO_x, NO_y, O₃, and CO measured during MINOS 2001

The mean altitude profiles of NO_x, NO_y, O₃ and CO measured during the 14 MINOS flights are shown in Fig. 2. The averaged tropospheric data (defined as O₃ < 160 ppbV) including 1 standard deviation (±1σ) are plotted. The highly variable NO_x data in the boundary layer with average volume mixing ratios (VMR) of about 0.4 ppbV decrease with altitude to about (0.04±0.03) ppbV in the free troposphere between 4–8 km. Above 8 km altitude the NO_x VMR increases again. Mean NO_y VMRs in the boundary layer were about (1.5±1.0) ppbV during the MINOS campaign. These data decrease with increasing altitude to about (0.5±0.4) ppbV in the free troposphere and increase again slightly towards the tropopause. The average O₃ mixing ratios measured during the MINOS campaign up to about 8 km altitude range between 60 and 80 ppbV and increase slightly at higher altitudes. The mean VMRs of CO decrease from roughly (150±30) ppbV in the boundary layer to (100±20) ppbV at 4 km altitude. From the lower to the upper free troposphere the CO VMRs slightly decrease from approximately 100 ppbV.

According to the classification presented in Emmons et al. (2000) the shapes of the NO_x, O₃ and CO profiles measured during MINOS 2001 resemble those influenced by industrial pollution and/or biomass burning.

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3.2 Comparison with other aircraft measurements

To reveal differences and similarities of the MINOS 2001 dataset with other northern extratropical campaigns, i.e. under different pollution levels in the Atlantic and European continental region, the MINOS data from the troposphere were compared with tropospheric data from earlier campaigns. The campaigns used for the comparison are

- (a) the SIL 1996 campaign of the German national programme “Schadstoffe in der Luftfahrt” (SIL 1996) (e.g. Schumann 1998, 2002) in which data were sampled in the North American flight corridor based out of Prestwick, Scotland (Ziereis et al., 1999).
- (b) the POLINAT-2 campaign with 14 flights conducted in September/October 1997 from Shannon, Ireland, with the main focus to study the impact of air traffic on the composition of the atmosphere at altitudes between 9 and 13 km (Ziereis et al., 2000a; Schlager et al., 1999; Schumann et al., 2000, <http://www.pa.op.dlr.de/polinat>).
- (c) the DLR EXPORT 2000 campaign with 9 flights based out of Oberpfaffenhofen, Germany, in July/August 2000 over central Europe with the aim to study the export of pollutants out of source regions over Europe.

The direct comparison of the NO_x , NO_y , O_3 , and CO profiles is shown in Fig. 3. To obtain a clearer picture of the comparison, the MINOS data are plotted as the average values with the corresponding standard deviations, whereas for the other campaigns only the averages are printed. It will be highlighted in the text whenever very high or low standard deviations were observed.

NO_x (Fig. 3A). At first glance the observed NO_x VMRs from the EXPORT 2000 campaign seem to be higher than the data from all other campaigns. However the EXPORT 2000 data up to about 6 km altitude do also show strong variations and the

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1σ standard deviations (not shown in the plot) are extremely high and close to 100% of the absolute values. This indicates extreme variations of the NO_x mixing ratios due to fresh emissions and convection over central Europe in summer. Comparing the POLINAT-2 and SIL 1996 NO_x profiles with the MINOS data reveals that the MINOS NO_x VMRs are slightly higher above ≈ 8 –10 km. Again, according to the classification given in Emmons et al. (2000) the profiles from both datasets, EXPORT 2000 and MINOS 2001, can be best described as “profiles influenced by industrial emissions and/or biomass burning”.

NO_y (Fig. 3B). In contrast to the high variability of the NO_x data the EXPORT 2000 NO_y data are smoother and exhibit lower standard deviations (not shown). However, the average total NO_y profiles from these campaigns are almost identical to the MINOS data, at least up to altitudes of about 8 km. This shows, that despite of the different airmass origins and transport times during the different campaigns, the average volume mixing ratios at different altitudes are very similar. However, compared to the MINOS data the POLINAT-2 NO_y data are almost 0.5 ppbV lower in the upper troposphere.

O_3 (Fig. 3C). Compared to the other campaigns the mean MINOS ozone mixing ratios are approximately 10–20 ppbV higher in the lower troposphere, but are similar to the measurements during EXPORT 2000 in the upper troposphere. The SIL 1996 and POLINAT-2 datasets indicate about 20 ppbV lower ozone values in the middle and upper troposphere up to altitudes of about 11 km. According to Emmons et al. (2000) the profiles from all campaigns can best be described as influenced by industrial pollution.

CO (Fig. 3D). At altitudes above 6 km the CO mixing ratios from the different datasets are all approximately 100 ppbV and are all within one standard deviation of the MINOS 2001 data. Below these altitudes the MINOS data are up to about 50 ppbV higher than during the other campaigns with a maximum slightly above 1 km altitude. The EXPORT 2000 data show an almost identical profile but with lower absolute concentrations. The POLINAT-2 profile deviates below 6 km with much lower values between 1 and 3 km and an increase again towards 6 km altitude, where all profile are within the scatter of the MINOS data.

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In summary, according to Emmons et al. (2000) the trace gas profiles of the two campaigns conducted over Europe, MINOS 2001 and EXPORT 2000, do show the same features as other data from areas with major industrial pollution. In the case of the EXPORT 2000 campaign fresh emissions lead to high variability in the NO_x data.

The profiles from SIL 1996 and POLINAT-2 do not show the “industrial profile features” so pronounced. However, in the free troposphere the volume mixing ratios of the trace gases were almost identical during all campaigns. From Figs. 3C and 3D it is also evident that O_3 and CO levels in the lower troposphere over the Mediterranean Sea are markedly higher than over central Europe during the same season.

3.3 Trace gas correlations

3.3.1 Mean correlations during the MINOS 2001 flights

In addition to the mean VMR altitude profiles the altitude dependences of the mean correlations between O_3 and NO_y , O_3 and CO, CO and NO_y , and NO_x and NO_y in ppbV/ppbV were calculated from the MINOS dataset containing the 10 s averages of all flights. These correlations represent the slopes of linear regressions in the plots between two species and are to some degree representative for the origin of the sampled air masses, see below (e.g. Murphy et al., 1993).

The altitude profiles of the correlations were calculated in altitude bins of 200 m and in steps of 50 m, i.e. the first correlation is calculated in the 0–200 m bin, the second correlation in the range 50–250 m, and so on. The expressions given for the slopes and the errors of the slopes are, for instance, given in Försterling and Kuhn (1971).

The results of the calculations are shown in the four panels of Fig. 4 as (a) the correlations themselves, (b) the r^2 value and (c) the number of experimental data points used to calculate the correlations.

$\Delta[\text{O}_3]/\Delta[\text{NO}_y]$. Figure 4A shows the altitude profile of the most prominent correlation between ozone and the total reactive nitrogen species NO_y . The $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ data show a steady increase with altitude from values below 10 in the boundary layer up

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to 150–220 in the upper troposphere at about 13 km. However, r^2 indicates only poor correlations up to about 4 km altitude, whereas the data are well correlated above 4 km.

These observed ratios fit well into the range of literature values of which a selection is summarized in Table 1. It should be noted that stratospheric ozone research predominantly revealed an almost constant $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ ratio of ≈ 330 in the lower stratosphere below 20 km and for $> 10^\circ$ latitude on both hemispheres and of ≈ 1000 in the tropical stratosphere for $< 10^\circ$ latitude (Murphy et al., 1993; Fahey et al., 1996; NASA, 1993). The robustness of this ratio is explained by the similar chemical lifetimes of the two species in the lower stratosphere in combination with transport and mixing processes (e.g. Murphy et al., 1993). Due to the entrainment of stratospheric air into the troposphere ratios of up to 150 to 250 have been found e.g. at the Mauna Loa Observatory (3400 m a.s.l.) and between 3–6 km altitude above Alaska (Atlas et al., 1996; Wofsy et al., 1992; Hübler et al., 1992a). Furthermore, the values of about 83 at altitudes between 5–11 km measured by Ridley et al. (1994) over New Mexico agree well with the MINOS data of 50–100 between 4–10 km altitude. Although the MINOS correlations in Fig. 4A are not very significant in the boundary layer, the data also agree well with the O_3/NO_y slopes of approximately 10 near the surface as measured by other groups at these altitudes in photochemically aged rural air masses (e.g. Tov et al., 1997; Buhr et al., 1996; Trainer et al., 1993; Olszyna et al., 1994; Ridley et al., 1994).

Buhr et al. (1996) and Ridley et al. (1994) pointed out that if a correlation between ozone and NO_y exists in the lower and middle troposphere the air masses are either influenced by downward mixing of upper tropospheric or lower stratospheric air and/or the air has been photochemically aged and the ratio provides a measure for the “photochemical age” of the air mass. Therefore, many authors have also used the slope of $\Delta[\text{O}_3]/\Delta[\text{NO}_z]$ with $[\text{NO}_z] = [\text{NO}_y] - [\text{NO}_x]$ as an estimate for the upper limit of the ozone production efficiency in photochemically aged polluted air masses (Carpenter et al., 2000; Liu et al., 1987; Trainer et al., 1993; Olszyna et al., 1994; Tanner et al., 1998). The number of ozone molecules found per number of NO_x molecules oxidized

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to NO_z was found to be in the range 4 to 30 in the free troposphere in spring during the FREETEX 98 campaign over the Alps (Carpenter et al., 2000). Figure 5 shows the $\Delta[\text{O}_3]/\Delta[\text{NO}_z]$ altitude profile inferred from the MINOS dataset which shows up to a factor of 2 higher values of about 50–80 in the free troposphere between 4–10 km over the Mediterranean in summer indicating a much higher ozone production efficiency during the MINOS campaign than during the FREETEX measurements, being more in line with airborne measurements during the SOS Nashville Ozone Study 1995 of approximately 60 (Tanner et al., 1998).

$\Delta[\text{O}_3]/\Delta[\text{CO}]$. Another correlation which is often used to estimate the photochemical ozone production rates during the transport of air masses is the ratio between ozone and the relatively long-lived anthropogenic tracer CO which has a lifetime of about 1 month in the free troposphere in summer (Chin et al., 1994; Parrish et al., 1993a). Parrish et al. (1993a), for instance, used the slope of the O_3/CO regression line from several ground stations downwind from the North American emission sources to estimate the amount of photochemically produced O_3 exported to the free troposphere over the North Atlantic Ocean.

The altitude profile of the $\Delta[\text{O}_3]/\Delta[\text{CO}]$ correlation during the MINOS 2001 flights is plotted in Fig. 4B. Relatively significant values of approximately 0.1 to 0.2 are found in the boundary layer. The ratio increases between 4 and 5 km up to values of about 1 which may indicate ozone production (see below). Between 5–9 km, almost no correlation is found. In line with the expected anticorrelation of the two species in the stratosphere, the ratio becomes significantly negative in the upper troposphere (e.g. Herman et al., 1999; Fischer et al., 2000). As shown in Table 2, which gives an overview of literature values, the slope of the O_3/CO correlation was found to be amazingly constant in the planetary boundary layer and lower troposphere with typical values ranging from approximately 0.2 to 0.4 (McGovern et al., 1996; Parrish et al., 1993a; Wofsy et al., 1992; Buhr et al., 1996; Carpenter et al., 2000; Chin et al., 1994; and references therein). This is slightly higher than the values derived from the MINOS dataset in the planetary boundary layer, but lower than the MINOS correlations of ~ 1 between 4–

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6 km altitude where, as indicated above, photochemical ozone production is expected (Lelieveld et al., 2002).

$\Delta[\text{CO}]/\Delta[\text{NO}_y]$. A compact correlation between CO and NO_y indicates a common source of these two combustion products in the troposphere. Wofsy et al. (1992), for instance, used this ratio in connection with the O_3/CO ratio to categorize plumes influenced by biomass burning. In their study $\Delta[\text{CO}]/\Delta[\text{NO}_y]$ values of 120 were found in a haze layer influenced by biomass burning which was well in the range of 25–350 of this ratio expected from a literature survey (Wofsy et al., 1992; and references therein). Buhr et al. (1996) found a ratio of 12 over a polluted area in the USA. While no correlation is expected in the “clean” free troposphere, an anticorrelation is expected in stratospheric air masses (Hübner et al., 1992a, 1992b). Panel C of Fig. 4 shows the altitude dependence of the $\Delta[\text{CO}]/\Delta[\text{NO}_y]$ ratio derived from the data of the MINOS 2001 flights. Values with $r^2 > 0.5$ are in the range of 40–50 in “layers” below 5 km altitude. However, it should be noted that the CO vs NO_y ratio depends strongly on single “pollution plumes” as observed during many of the MINOS 2001 flights (see below), and the average $\Delta\text{CO}/\Delta\text{NO}_y$ over all flights should not be “overinterpreted”. As expected, the ratio becomes strongly negative when the air is influenced by the stratosphere in the upper troposphere.

$\Delta[\text{NO}_x]/\Delta[\text{NO}_y]$. Panel D of Fig. 4 shows the altitude profile of the slope of the NO_x vs NO_y ratio, which – because oxides of nitrogen from combustion processes and lightning are mainly emitted as NO_x ($=\text{NO}+\text{NO}_2$) and are afterwards converted into NO_y species – can be used as a measure of the age of emissions. A quite common definition for the ratio in photochemically aged air is e.g. a ratio of $\Delta[\text{NO}_x]/\Delta[\text{NO}_y] < 0.3$ (e.g. Tov et al., 1997; and references therein). The MINOS dataset shows remarkably high values of 0.3–0.8 in the lowest 500 m indicating fresh emissions. Values with $r^2 > 0.5$ are about 0.6 between approximately 200 and 300 m altitude. In the free troposphere up to about 10 km the correlation coefficients are generally below 0.4.

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3.3.2 Correlation analyses during single flights and in single plumes

For a more detailed analysis of single plumes during the MINOS flights the correlations between the trace gases were calculated as linear least-squares-fits (a) in time intervals of 600 s during the flight, (b) in altitude bins of 750 m, and (c) for dedicated analyses of single plumes which could be traced back by trajectory calculations (Traub et al., this issue). For each set of calculations one case study will be discussed in the following.

The absolute values of a correlation was plotted only when the r^2 -value of the calculation exceeded 0.5. The number of available data points used for one correlation value was in the range 15–200. It is important to note that the absolute values of the correlations change with the size of the intervals used for the calculations, e.g. the altitude ranges and the time intervals. The resolution of the time and altitude correlations for these investigations was chosen to be 60 s and 100 m, respectively, e.g. the altitude correlations were calculated in bins between 0–750 m and 100–850 m, etc.

(a) Case Study 1 Sampling of stratospheric air along the flight track. According to the meteorological forecast for 16 August 2001 there was a region with high potential vorticity (> 2 PVU) at the 300 hPa level (≈ 9 km altitude) over north-west of Crete and partially over the Greek mainland indicating a low tropopause. Since very high tropopause heights (> 15 km) prevailed during most of the campaign (see Roelofs et al., this issue) and the Falcon aircraft only has a ceiling altitude of about 13 km, the goal of MINOS flight 8 on 16 August 2001 was to try to sample stratospheric air in this region.

Due to lacking CO data at the beginning of the flight Fig. 6 only shows the time series of the correlation analysis between 12:15 and 14:45 UTC. Two penetrations of stratospheric air masses can unambiguously be identified at 12:50–12:55 UTC and $\approx 13:25$ UTC by high values of the $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ and negative values of the $\Delta[\text{O}_3]/\Delta[\text{CO}]$ ratio. During these events no correlation between NO_x and NO_y is observed, whereas – as expected – the CO/NO_y ratio is negative.

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Due to fresh emissions in the boundary layer the NO_x/NO_y ratio increases during the descent at the end of the flight at approximately 14:20 UTC with the slope of $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ at typical boundary values of 11 ± 2 .

(b) Case study 2 Altitude profile of trace gas correlations during one flight. The objective of flight 2 of the MINOS campaign on 3 August 2001 was to observe forecasted pollution from Eastern Europe at lower flight altitudes and to capture expected outflow from the Asian monsoon region at higher altitudes, as shown in Fig. 1. The altitude dependence of the correlations measured over the northern Aegean Sea over Lesbos is shown in Fig. 7, indicating the sources of the measured trace gases.

In the boundary layer below 2 km altitude fresh emissions can unambiguously be identified by high $\Delta[\text{NO}_x]/\Delta[\text{NO}_y]$ ratios and a slightly negative slope of $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$. The $\Delta[\text{O}_3]/\Delta[\text{CO}]$ correlations at these altitudes reveal typical boundary layer values below 1. In addition, the good correlation of $\Delta[\text{CO}]/\Delta[\text{NO}_y]$ indicates common sources of these two species. Just below 3 km altitude the $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ ratio increases sharply in connection with negative $\Delta[\text{O}_3]/\Delta[\text{CO}]$ and $\Delta[\text{CO}]/\Delta[\text{NO}_y]$ correlations. This is a strong indication for air masses of stratospheric origin being transported into the lowest part of the free troposphere below 3 km into a very thin layer.

Between 6 and 7 km altitude enhanced $\Delta[\text{O}_3]/\Delta[\text{CO}]$ ratios are observed, whereas the other species do not correlate, which may indicate O_3 production during transport. Other interesting features are the relatively constant and low $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ and $\Delta[\text{O}_3]/\Delta[\text{CO}]$ ratios indicating boundary layer air, together with $\Delta[\text{NO}_x]/\Delta[\text{NO}_y]$ ratios exceeding 0.2 at approximately 11–12 km which, according to the forecasts in Fig. 1, may be associated with the Asian monsoon outflow.

In order to verify the origin of the air masses back trajectory calculations were performed. Figure 8 shows the 1-min averaged trajectory analyses for flight 2 during the time when the northern vertical profile was flown between 08:30 and 09:05 UTC in steps of 5 minutes. Figure 8A shows the longitude-latitude plot of the trajectories, Figure 8B shows the altitudes of the trajectories as a function of the travel time of the air parcels. As expected, the trajectories in the upper troposphere originate from

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the Asian monsoon region (Fig. 8A). The trajectories ending at altitude levels of approximately 6 km originate from the North-American continent subsiding from 8 to 6 m during the previous 10 days (with enhanced O_3/CO ratios) indicating that the air was being photochemically processed. Air masses with trajectories ending in the boundary layer have picked up fresh pollution from north-east Europe about one week earlier.

A notable trajectory ending at approximately 3 km altitude (08:59 UTC) originated from the upper troposphere at ≈ 10 km ten days before it crossed the Falcon flight track, giving rise to the very clear signature of stratospheric air in Fig. 7 at a remarkably low altitude. In contrast to the other trajectories in Fig. 8, this air parcel (08:59 UTC) did not travel very far and stayed over the Mediterranean during the previous 10 days.

Even without further knowledge about the origin of these air masses and the meteorological situation, the stratospheric signature is unambiguous.

(c) Single plume correlations During the 14 MINOS flights numerous plumes at different flight altitudes have been captured. An overview of the correlations in the single plumes is given in Table 3. The origins of the single plumes in the different altitude regimes could be identified from the trajectory analyses described by Traub et al. (this issue).

As an example Fig. 9 shows the altitude profiles of the analyzed trace gases of MINOS flight 9 on 17 Aug. 2001, measured during a step profile flown south of Crete. It should be noted that at the altitudes with large scatter of the data, i.e. at 2.4 km, 3.7 km, 5.8 km, 8.5 km, and 11.2 km, the aircraft flew long flight legs at constant altitude and sampled several different air masses.

From the surface up to about 2.5 km the influence of polluted boundary layer air is clearly visible in the NO_x , NO_y , and CO data. The data in the free troposphere appear relatively smooth, except for an enhancement of O_3 and NO_y between 6 and 7 km altitude. However, the most striking feature during this flight is the enhancement of O_3 , NO_x , and NO_y at constant CO mixing ratios at altitudes between 9 and 10 km indicating a layer of aged air masses. Figure 10 shows the single correlation plots of the trace gas measurements in this plume. All ratios except $\Delta O_3/\Delta CO$ exhibit high correlation coefficients.

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It is also worth looking at the intercepts in the different plots. The $\Delta[O_3]/\Delta[NO_y]$ fit intercepts the y axis at (75 ± 5) ppbV ozone indicating enhanced O_3 in the free troposphere which may be due to photochemical production and/or mixing with stratospheric air. Due to the poor correlation between O_3 and CO the intercept is quite uncertain with values of (34 ± 24) ppbV ozone at negligible carbon monoxide. The reason for the slightly negative intercept of the NO_x vs NO_y plot is the $\pm 25\%$ uncertainty associated with the calculation of the NO_x mixing ratios (see Sect. 2).

The majority of the trajectories ending at altitudes between 9–10 km during this flight indicate that these air masses started 5 days earlier from the west coast of North America ($\approx 52^\circ N$, $40^\circ W$) at about 11 km altitude, travelling over the North Atlantic Ocean to the Mediterranean region, slightly descending from north-easterly directions.

(d) Overview and comparison with earlier studies In the planetary boundary layer (PBL) the average $\Delta[O_3]/\Delta[NO_y]$ correlations (see Sect. 3.2.1) and the data from the single plume case studies in Table 3 agree well. The derived value of about 10 in the PLB from this study is in line with the findings in the literature, as given in Table 1. In the free troposphere the larger $\Delta[O_3]/\Delta[NO_y]$ ratio is reflected in the MINOS 2001 as well as in the literature data. However, the literature values up to ≈ 11 km altitude show a variation in the range 20–250 whereas the MINOS correlations vary within 20–100. This could be due to the fact that the tropopause height over the Mediterranean during MINOS was quite high (see Fig. 1 and Roelofs et al., this issue) and downward mixing of stratospheric ozone down to the ceiling altitude of the Falcon aircraft (≈ 13 km) was not very efficient. An additional explanation for the relatively low values of O_3 vs NO_y in the upper troposphere during MINOS is the influence of the Asian outflow carrying relatively fresh emissions ($NO_x/NO_y \geq 0.3$) in these altitudes (Scheeren et al., this issue). The measured lower stratospheric value for the O_3/NO_y ratio of about 130 in Table 3 is also a little lower than expected from most of the former studies in Table 1, but in excellent agreement with the values given in Lerner et al. (1994).

The comparison of the hardly significant O_3/CO slopes found during MINOS in Table 3 and former studies (Table 2) shows very good agreement in the boundary layer

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and in free tropospheric air masses. However, whereas Fischer et al. (2000) did not find any correlation in the troposphere during the STREAM 97 campaign, we find a value of $\Delta[\text{O}_3]/\Delta[\text{CO}] = 2.6$ at an altitude between 10–11 km in one of the North Atlantic/North American plumes during MINOS. In line with the findings of Fischer et al. (2000) a negative O_3/CO ratio was found in stratospherically influenced air masses.

The CO/NO_y slopes found in single plumes in this study are well in the range of the data given in the literature, i.e. mainly positive correlations in the troposphere and an anticorrelation in the stratosphere.

In summary, it was found that the trace gas correlations calculated for the MINOS 2001 dataset, both the absolute values and the altitude profiles, are in the range of the data described in the literature. The absolute values of the correlations at different altitudes can therefore be regarded to be more typical for an altitude range than for the origin of the air mass. One possible explanation for the minor differences between the literature and MINOS 2001 data is the exceptionally high tropopause and the Asian monsoon outflow events during the MINOS campaign over the Mediterranean. Furthermore, in this study the origin of stratospheric air could unambiguously be identified by correlation analyses.

4 Summary and conclusions

We presented mean altitude profiles of NO_x , NO_y , O_3 , and CO as measured by the DLR Falcon during the MINOS 2001 campaign over the Mediterranean in August 2001, and compared with data from other aircraft campaigns. The SIL 1996 (North Atlantic flight corridor), the POLINAT-2 (North Atlantic flight corridor), and the EXPORT 2000 (central Europe) campaigns were conducted at different latitudes and seasons. It was found that at least the MINOS NO_y , O_3 , and CO mixing ratios in the free troposphere between 4–8 km are very similar to those measured during the EXPORT 2000 campaign. During the MINOS campaign it was found that the main influence at these altitudes came from the North Atlantic and from North America (Lelieveld et al., 2002) with the mean

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mixing ratios showing very small scatter (standard deviations). However, compared to the other campaigns the MINOS O_3 and CO volume mixing ratios were significantly higher in the boundary layer, by about 20 ppbV and 50 ppbV, respectively. According to Emmons et al. (2000, and references therein) the shape of the trace gas vertical profiles from these two campaigns can best be described as “influenced by industrial pollution and/or biomass burning”.

In Sect. 3.2 the $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$, $\Delta[\text{O}_3]/\Delta[\text{CO}]$, $\Delta[\text{CO}]/\Delta[\text{NO}_y]$, and $\Delta[\text{NO}_x]/\Delta[\text{NO}_y]$ trace gas correlations were calculated for the MINOS 2001 campaign. It was found that, within the scatter of the data, the overall/average altitude profiles of the correlations compared well with data from a literature survey. The analysis of the mean vertical correlation profiles as measured during MINOS 2001 does therefore not reflect the special meteorological conditions and air mass origins over the Mediterranean in summer (e.g. Lelieveld et al., 2002; and references therein) but reveals a more general feature of the troposphere which is also found in other regions in the northern hemisphere.

However, case studies of correlation analyses during single flights at different altitudes allowed the unambiguous identification of air masses influenced by the stratosphere. The origins of other plumes captured during MINOS 2001 could only be identified with the help of back trajectories. The overall analysis of the times series and altitude profiles of the correlations during single flights in connection with back trajectory data revealed signatures from stratospheric air, the Asian monsoon outflow, and European pollution.

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Table 1. Survey of $\Delta[\text{O}_3]/\Delta[\text{NO}_y]$ correlations at different altitudes from field measurements. Whenever available the r^2 are given in parentheses

Altitude	$\Delta[\text{O}_3]/\Delta[\text{NO}_y]$	Area	Comment	References
PBL	6-10 (0.73-0.9)	Mediterranean, Israel	photochemically aged air, rural site, no correlation in fresh plumes	Peleg et al. 1994
PBL	10.9 (0.98)	Mediterranean, Israel	transported aged polluted air, NO_y limited	Tov et al. 1997
PBL	≈ 10	USA, Gulf of Maine		Buhr et al. 1996
PBL	no corr.	marine air, < 600 m		Hübner et al. 1992b
PBL	≈ 11	US ground stations	photochemically aged air masses	Trainer et al. 1993
PBL	10	continental USA stations		Olszyna et al. 1994
2-2.5 km	≈ 33	New Mexico		Ridley et al. 1994
2-3 km	≈ 22	Alaska	haze layer, forest fire emissions	Wofsy et al. 1992
> 3 km	≈ 95	Mauna Loa Observatory + aircraft measurements	free troposphere, data from different campaigns > 3 km	Hübner et al. 1992a
3.4 km	185	Mauna Loa Observatory	remote free troposphere	Atlas et al. 1996
3-6 km	158-173	Alaska	"background"	Wofsy et al. 1992
4.4-6.1 km	167-250	marine and continental USA	free troposphere, marine air	Hübner et al. 1992b
5-11 km	≈ 83	New Mexico		Ridley et al. 1994
FT & LS	130 \pm 3.4 (0.99)	England	1990/91, summer campaigns	Lerner et al. 1994
LS	≈ 185 (0.97)	37-57deg N		Singh et al. 1997
LS	189-256	> 60 deg N	POLSTAR 1, 1997	Ziereis et al. 2000a
LS	278-417	> 60 deg N	POLSTAR 2, 1998	Ziereis et al. 2000a
LS	≈ 200 -250	40-90 deg N, 10-12 km alt.		Weinheimer et al. 1993
LS	≈ 200	N_2O :170-310 ppbV		Chang et al. 1996
S	≈ 1000	$\leq 10^\circ\text{N/S}$, 50-70 hPa	(18-20 km)	Fahey et al. 1996, Murphy et al. 1993
	≈ 330	$\geq 10^\circ\text{N/S}$, 50-70 hPa		

2014

Table 2. Survey of $\Delta[\text{O}_3]/\Delta[\text{CO}]$ correlations at different altitudes from field measurements. Whenever available the r^2 are given in parentheses

Altitude	$\Delta[\text{O}_3]/\Delta[\text{CO}]$ (ppbV/ppbV)	Area	Comment	References
PBL	0.34 (0.86)	Mace Head, Ireland	no biomass burning, in case of biomass burning, no correlation was found.	McGovern et al. 1996
PBL	-0.345±0.025 (0.42)	Barrows, Alaska	dark period, air from Sibiria	Harris et al. 2000
PBL	0.3	North America	photochemically aged air	Chin et al. 1994 + ref's therein
PBL	0.22-0.29	Atlantic coast of Canada		Parrish et al. 1993
PBL 0-0.8 km	0.29 (0.76)	Gulf of Maine, New England		Buhr et al. 1996
PBL 0.8-1.5 km	0.32 (0.50)	Gulf of Maine, New England		Buhr et al. 1996
1.5-4.5 km	0.015-0.093	Amazonia	biomass burning plumes	Andreae et al. 1988
2-3 km	≈ 0.21	Alaska	haze layers, forest fire plumes	Wofsy et al. 1992
3-6 km	no corr.	Alaska	Background air	Wofsy et al. 1992
FT 3.58 km	0.28 (0.67)	Jungfraujoch	Freetex'98	Carpenter et al. 2000
< 6.5 km	0.58	USA	increasing with altitude	Carrol et al. 1990
< 6.5 km	0.37	Eastern Pacific	increasing with altitude	Carrol et al. 1990
Troposphere	no corr.		STREAM 97	Fischer et al. 2000
Stratosphere	≈ - 24		STREAM 97	Fischer et al. 2000

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Table 3. Overview of the single plume events that showed correlations ($r^2 > 0.5$) between the analyzed trace gases. The r^2 are given in parentheses. (^(*) 12:50–13:30 UTC)

Altitude	$\Delta[\text{O}_3]/\Delta[\text{NO}_x]$ (r^2)	$\Delta[\text{O}_3]/\Delta[\text{CO}]$ (r^2)	$\Delta[\text{CO}]/\Delta[\text{NO}_x]$ (r^2)	$\Delta[\text{NO}_3]/\Delta[\text{NO}_x]$ (r^2)	Flight #	Origin
PBL: ≈ 0.1 km	10 ± 1 (0.91)	0.22 ± 0.02 (0.63)	36 ± 2 (0.83)	0.19 ± 0.003(0.97)	13	Western European Air
PBL: < 2 km	7 ± 1 (0.65)	---	---	0.29 ± 0.03(0.60)	14	---
PBL: < 2 km	10 ± 1 (0.56)	---	---	---	9	Eastern European Air
PBL: < 1.5 km	12 ± 1 (0.57)	---	---	---	8	---
PBL: < 1.5 km South	8 ± 1 (0.51)	---	---	---	7	---
FT: 3-7 km North	22 ± 1 (0.77)	0.23 ± 0.02 (0.70)	92 ± 2 (0.95)	---	7	---
FT: 3-7 km South	66 ± 4 (0.86)	---	---	---	7	---
FT: 3-8 km	72 ± 6 (0.54)	---	---	---	3	North Atlantic Air
FT: 6-9 km	37 ± 1 (0.75)	---	---	0.13 ± 0.01 (0.64)	9	Mixture: West + East
FT: 7-10 km	49 ± 2 (0.81)	---	---	---	10	North American+ N. Atlantic
FT: 6-9 km	40 ± 2 (0.81)	---	---	---	13	---
UT: 10-11 km	44 ± 1 (0.94)	2.6 ± 0.1 (0.89)	16 ± 1 (0.86)	---	13	---
UT: 9-10 km	25 ± 4 (0.74)	---	12 ± 1 (0.80)	0.21 ± 0.01 (0.96)	9	---
UT: 8-11 km	102 ± 5 (0.59)	---	---	0.24 ± 0.01 (0.58)	14	---
UT: > 10 km	59 ± 2 (0.73)	---	---	0.39 ± 0.02 (0.73)	1	Monsoon Outflow
UT: > 10 km	72 ± 2 (0.80)	---	---	0.30 ± 0.01 (0.76)	2	---
LS: 9.4 km ^(*)	133 ± 7 (0.75)	-7.1 ± 0.5 (0.64)	-14 ± 1 (0.63)	0.24 ± 0.02 (0.60)	8	Lower Stratospheric Air

2016

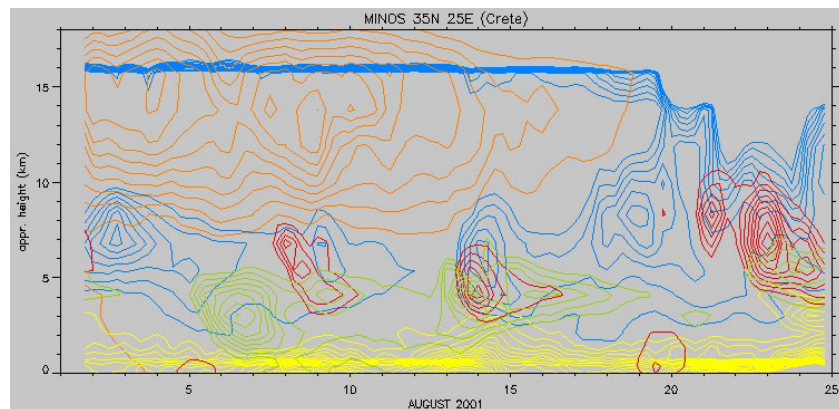


Fig. 1. Qualitative analysis of tracers originating from different regions as an altitude plot over Crete during August 2001, see Roelofs et al., this issue. Yellow indicates European tracers, blue reflects stratospheric influence, orange Asian tracers, and red and green North American and North Atlantic tracers, respectively.

2017

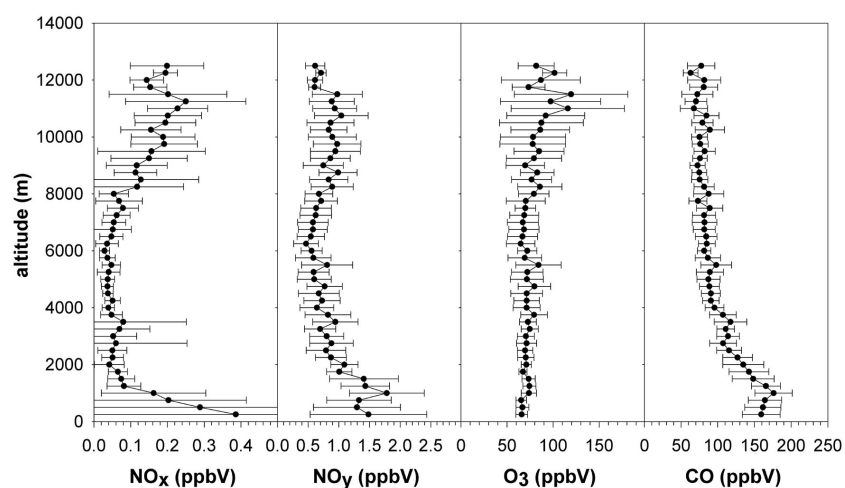


Fig. 2. Mean altitude profiles of NO_x , NO_y , O_3 , and CO ($\pm 1\sigma$) measured during the MINOS campaign in August 2001 over the Mediterranean Sea.

2018

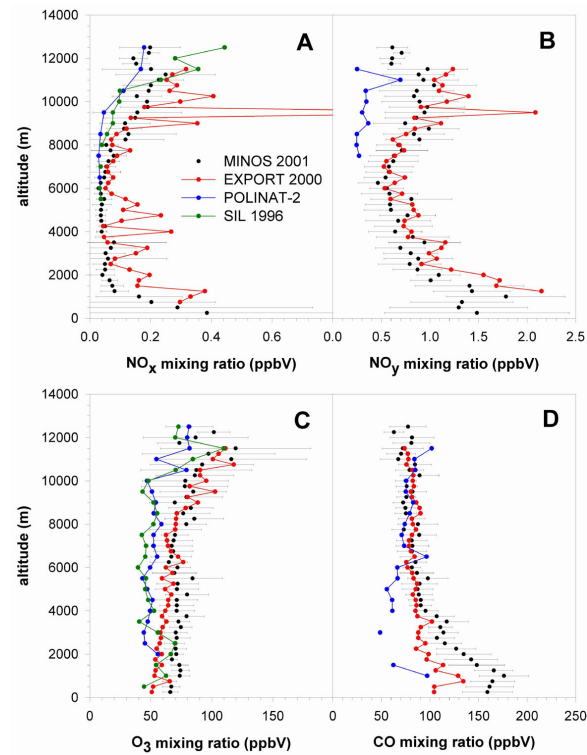


Fig. 3. Comparison of trace gas altitude profiles measured during the MINOS campaign with data from the EXPORT 2000, POLINAT-2, and SIL 1996 campaigns, see text for details.

2019

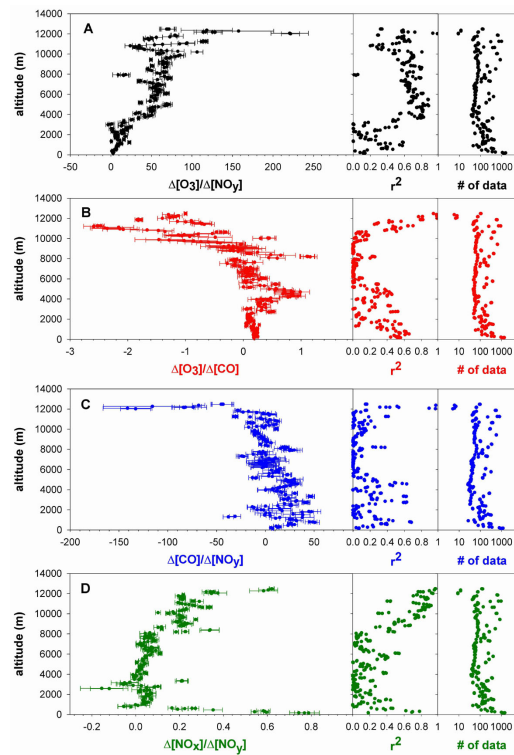


Fig. 4. Mean altitude profiles of the trace gas correlations calculated from the 14 MINOS 2001 flights over the Mediterranean. To the right the r^2 -value and the number of data points used for the calculation are given for the different altitudes.

2020

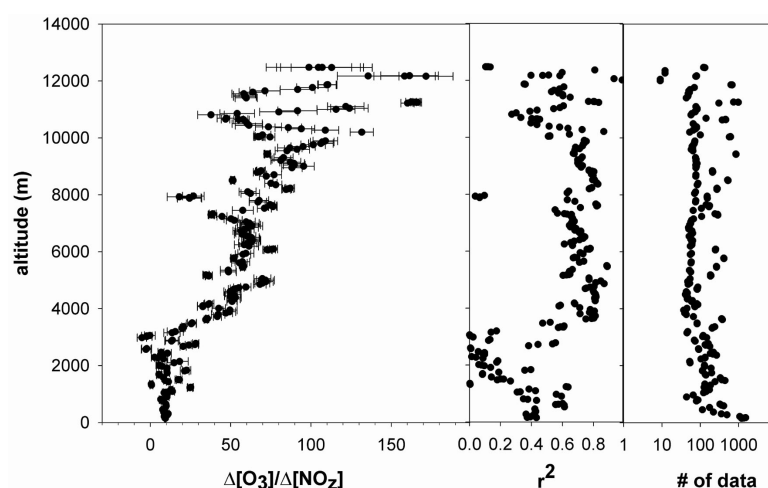


Fig. 5. Altitude profile of the O_3 vs NO_z ($=NO_y-NO_x$) correlation calculated from the MINOS dataset. To the right the r^2 -value and the number of data points used for the calculation are given for the different altitudes.

2021

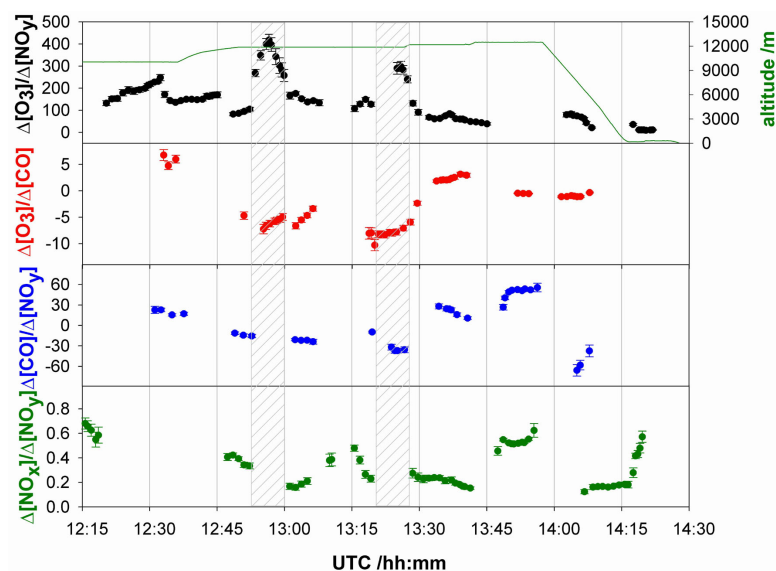


Fig. 6. Time series of the correlations calculated during the second part of MINOS flight 8 (16 August 2001) over the north-western Aegean Sea with the aim to sample the stratosphere at high altitude levels of the flight. The time intervals in which stratospheric air was sampled are highlighted.

2022

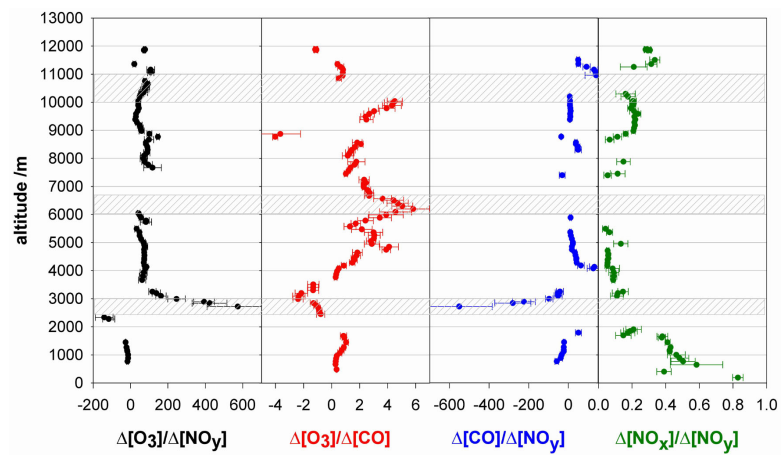


Fig. 7. Altitude profiles of the correlations during the northern vertical profiles of MINOS flight 2 (3 August 2001) over the northern Aegean Sea.

2023

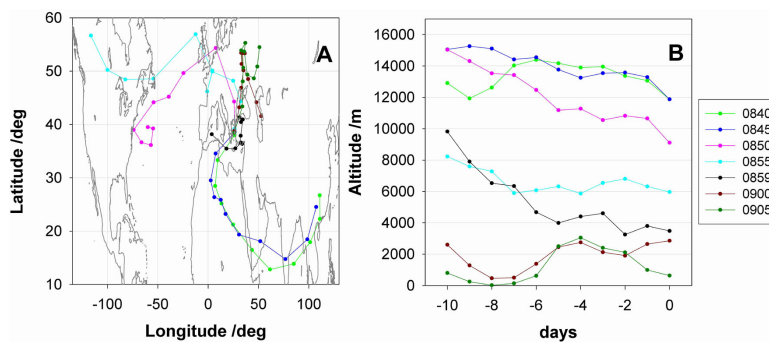


Fig. 8. Longitude-latitude plot of the trajectories for the northern profile of MINOS flight # 2 on 3 August 2001 (A). The trajectories end along the flight path of the Falcon aircraft. (B) shows the altitudes of these trajectories as a function of travel time.

2024

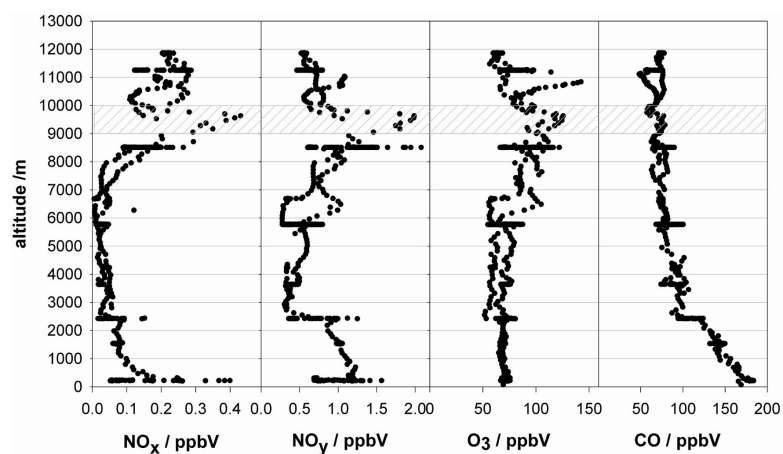


Fig. 9. Altitude dependence of the measured trace gas mixing ratios during MINOS flight 9 (17 August 2001). A remarkable feature is the layer between 9–10 km indicating aged air masses, see text for details.

2025

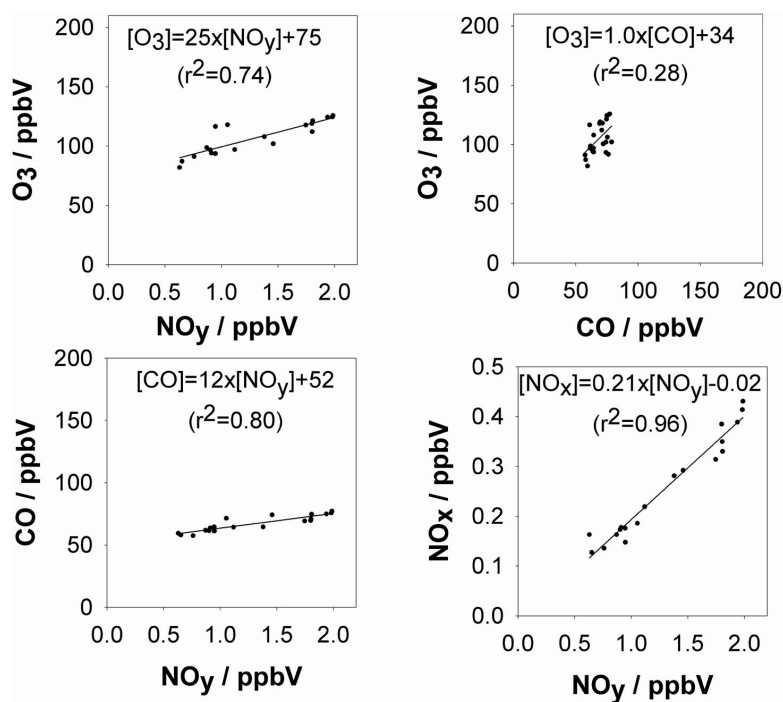


Fig. 10. Trace gas correlations for the plume between 9 and 10 km altitude of MINOS flight 9 (17 August 2001), see Fig. 9. All plots show high correlations except for $\Delta[\text{O}_3]/\Delta[\text{CO}]$. The uncertainties of the slopes and the intercepts are given in Table 3 and in the text, respectively.

2026